THE ROLE OF PHYSICAL FACTORS IN MASS TRANSPORT AND PHASE TRANSFORMATION IN INTERGRANULAR MELTS DURING COAL ASH SINTERING AND DEPOSIT DEFORMATION

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ABSTRACT

The role of physical properties of melts such as viscosity, diffusion, and surface–interfacial tensions in sintering and deformation mechanisms of ash deposits above the glass transformation temperature is discussed. The differential thermal analysis (DTA) technique was applied to measure glass transformation and crystallization temperatures. Sintering of selected coal ashes was performed as a function of temperature in air. The mechanical properties of sintered ashes were measured below and above T_g. It was found that a correlation exists between sintering propensities of amorphous ashes and plastic deformation of deposits above T_g, which both depend on the mass transport phenomena in the intergranular liquid phase.

INTRODUCTION

In combustion and gasification technologies a great need exists to define the lowest temperature at which the fouling propensity of fly ash on heat-exchange surfaces is maximally reduced. Numerous experimental studies have been reported in the literature that emphasize the role of interparticle melts in the sintering behavior of fly ashes. Using a quasichemical approximation, researchers were able at first to give a qualitative description of the liquid-phase composition that causes rapid deposit growth. Specific interactions between ash particles with dissimilar chemical compositions usually cause the formation of an interparticle silicate melt with a nonuniform structural composition, the unstable physical properties of which affect intergranular mass transport. The structural heterogeneity of silicate melts depends on two major contributions to the free energy of mixing: configurational entropy of mixing, which favors mutual miscibility, and dispersion forces, which energetically favor phase separation. A formulation of the chemical composition and structural homogeneity of melts to account for intergranular transport in the liquid phase is applied here. The preparation procedure for homogeneous aluminosilicates derived from coal ashes was described in an earlier article.[1] Mass transport through an intergranular liquid phase near and above the temperature of glass transformation, T_g, in sintering and superplasticlike deformation of ash deposits is described here.

HYSTERESIS IN MELT–CRYSTAL TRANSFORMATION AND GLASS TRANSFORMATION TEMPERATURE

Figure 1 illustrates the variation of Beulah slag viscosity with temperature, on cooling. The rapid increase of viscosity below the temperature of critical viscosity (T_c) is caused by slag crystallization.[2] Figure 2 shows the differential thermal analysis (DTA) results for Beulah glass and two more selected glasses derived from coal ashes on heating. The exotherms are caused by the formation of crystalline phases. Generally, hysteresis in the slag–crystal transformation manifests itself as a difference in crystallization temperatures on cooling of a melt and on heating of a glass. This effect does not suggest that melt transformation occurs at two different free energies. On cooling, the free energy of a supercooled melt is similar to that of nucleation and crystalline-phase growth on the liquidus. On heating, however, the additional energy for nucleation and further crystal growth of the same crystalline phase(s) comes from strain energy created during fast cooling and interfacial energy in the case of polycrystalline amorphous material. The strain energy results from the formation of an unrelaxed matrix during structural relaxation of the melt. The formation of a crystalline phase 1) in the bulk of the slag will increase its viscosity and simultaneously change its flow characteristics and 2) in an intergranular melt will increase deposit strength.[1]

The temperatures of glass transformation, T_g, on heating, are indicated in Figure 2. The ideal T_g corresponds to structural relaxation, at which the melt remains in equilibrium, and crystallization does not occur. This takes place only when the quench rate is high enough.[3] It has been demonstrated empirically that shear viscosity is of the order of 10^{13} poise at T_g, and various thermodynamic quantities such as compressibility, specific heat, and thermal expansion are discontinuous.[4] In this context, the glass transition is simply a reflection of the appearance of the elastic component. A remarkable aspect of glass transition is that it suggests changes in deposit behavior from brittle below T_g to ductile above T_g. This means that a glassy slag and/or intergranular amorphous phase will start to flow.

Figure 3 illustrates the variation in the crystallization temperature and temperature of glass transition with the base:acid ratio. Generally, both temperatures, T_c and T_g, increase with lowering base:acid ratio.

The T_g can be evaluated using an empirical equation [1] if the liquidus temperature of an aluminosilicate system is known:[5]

$$T_g/T_c \approx 2/3 \qquad [1]$$

Calculated temperatures of glass transformation for amorphous ash slags, included in Figure 3, correspond to those determined by DTA.

DENSIFICATION AND SUPERPLASTICLIKE DEFORMATION

Figure 4 illustrates changes in the apparent density of sintered amorphous coal ashes with temperature. The minimum on the curves corresponds to the maximum volume of deposits resulting from the volume of material and closed pores.[6] Usually, the densification process is defined as a pore filling by a liquid-phase flow and pore shrinkage, depending on the physical properties of the melt. The sintering process in Beulah and Montana ashes begins at about 700° and 750°C and occurs at temperatures lower than the glass transition temperatures, $T_g \approx 800°$ and $\approx 830°C$, respectively. This process seems to be caused by strain and interfacial energies stored in surface layers of unrelaxed ash particles, which enhance the diffusion coefficient of ions. Stress has long been known to affect the diffusion process in glass components. A quenched glass usually has a higher ionic transport rate than its crystalline form.

Figure 5 shows the compressive stress–strain relationship in sintered Illinois ash slag determined below and above the temperature of glass transformation, $T_g \approx 940°C$. Interestingly, the ash deposit is brittle below T_g and exhibits ductile properties above 900°C as a consequence of the disappearance of the elastic property of the intergranular amorphous phase. It is apparent that mean compressive stress decreases as the ash base:acid ratio increases (Figure 6). This suggests that the yield strength of the deposit depends on the thickness of the intergranular liquid phase and decreases with the increases in the base:acid ratio. Generally, the uniform yield (flow) stress as recorded on Figures 5 and 6 is attributable to superplasticlike deformation of materials, which is observed during stretching of a body as a large elongation without cracking. In glass ceramics, superplasticlike behavior may arise either by the viscous flow mechanism of intergranular layers or diffusion, which may be similar either to viscous[7] or to diffusional[8] creeps. Most silicate glasses containing modifying oxides are close to ideal elastic solids below the glass transition temperature.[9] There is, however, a small delay of elastic effect, likely resulting from the motion of alkali ions.

DISCUSSION

Intergranular mass transport in coal ashes sintered above the temperature of glass transformation (T_g) can be compared to that in capillarylike media that is based on viscous–diffusional mass transport.[10] In this model of liquid-phase sintering, the motion of the melt is caused by activated motion of the meniscus, which may occur either by viscous flow or by volume diffusion. The movement of the meniscus originates from the interface of atomic/ionic motion, creating a dynamic surface tension in the liquid phase. Intergranular mass transport through the liquid phase requires a sufficient quantity of melt, above some critical thickness, which may be provided by the dissolution of silicate from ash particles into the melt. In heterogenous systems, this can create gradients of chemical potential, possibly introducing nonequilibrium conditions.

Superplasticlike deformation in ash deposits may occur above the temperature of glass transformation (T_g). Two major independent factors allow superplasticlike deformation in a polycrystalline material with a liquid phase to occur. The first factor is a repetitive cycle of plasticity and dissolution of particle-to-particle connections; the second is compressive stress, which will segregate a small fraction of liquid to triple junctions.[11] Thus, the model of superplasticlike deformation of ash deposits above T_g seems to be similar to that of the transport of matter through the liquid phase in the liquid-phase sintering mechanism. The migration of intergranular melt is a response to the imposed gradients of hydrostatic pressure across the specimen caused either by surface tension, in the case of sintering, or by compressive stress, in case of superplastic deformation.

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TABLE 1. Composition of Coal Ashes (weight percent expressed as equivalent oxide)

| ID	Description	B:A	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	TiO$_2$	CaO	MgO	Na$_2$O	K$_2$O	P$_2$O$_5$
A	Beulah	0.64	27.5	15.0	16.3	1.6	24.8	5.9	8.1	0.1	0.6
B	NIPSCO	0.64	31.1	15.1	13.0	1.3	29.4	6.9	1.2	2.1	0.3
C	SUFCo	0.37	51.3	11.0	9.6	0.4	22.1	2.0	2.7	0.0	0.8
D	Montana Subbituminous	0.28	47.2	24.0	5.4	1.1	15.5	4.7	0.7	0.7	0.7
E	Pittsburgh 1	0.17	47.8	18.1	18.0	0.8	9.4	3.0	1.5	1.1	0.1
F	Pittsburgh 2	0.15	48.7	18.7	18.7	0.9	8.3	1.6	1.1	1.8	0.2
G	Illinois	0.12	48.6	23.1	14.3	1.2	5.6	1.6	0.5	3.1	0.3
H	Gascoyne	0.73	35.2	11.5	8.8	1.5	27.6	7.5	6.7	0.1	1.0
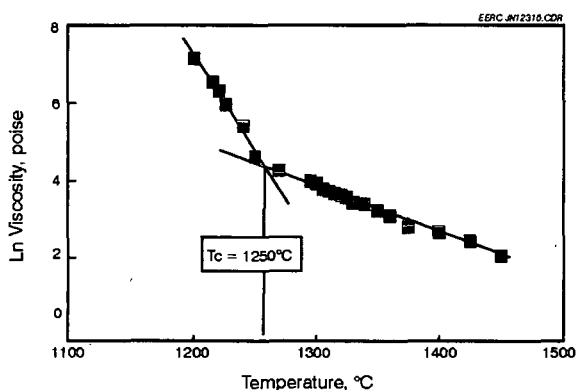
Figure 1. Logarithm viscosity–temperature relationship for Beulah ash slag, as determined on cooling.
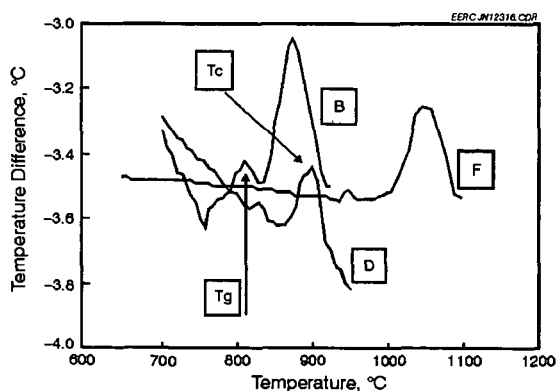

Figure 2. DTA curve of NIPSCO (B), Montana subbituminous (D) and Pittsburgh 2 (F) ash glasses, as determined on heating. DTA measurements were performed using a DuPont 2100 instrument in air at a heating rate of 8°C/min.
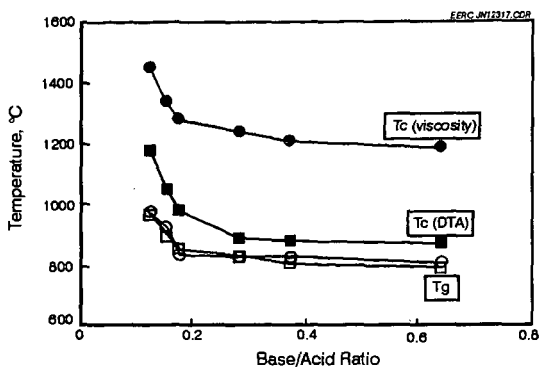
Figure 3. The relationship between the temperature of glass crystallization, glass transformation, and base:acid ratio in ash slags. The calculated values of T_g are represented by □. The chemical compositions of the coal ashes are listed in Table 1.
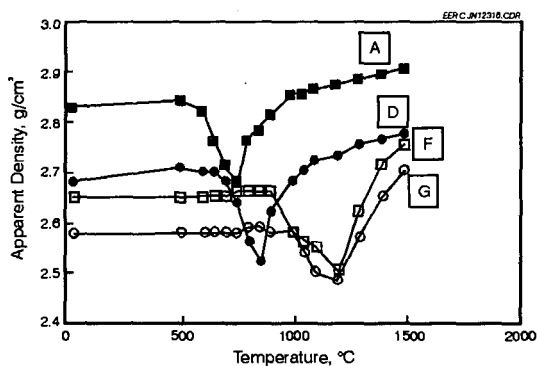

Figure 4. Dependence of apparent density upon sintering temperature for selected ash slags. The chemical compositions of the coal ashes are listed in Table 1.
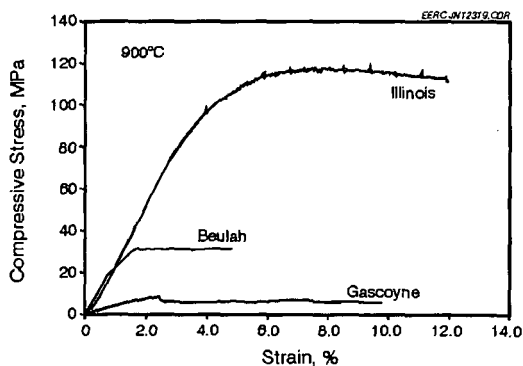

Figure 5. Compressive stress vs. strain in Illinois coal sintered at 1100°C for 20 hr in air. The deformation rate was $2 \cdot 10^{-5} \text{ m} \cdot \text{min}^{-1}$.
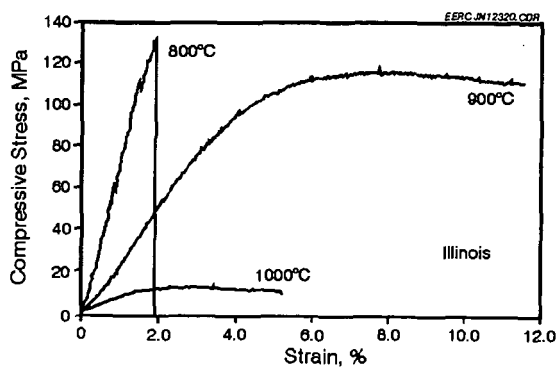
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Figure 6. Compressive stress vs. strain in Illinois, Beulah, and Gascoyne ashes sintered at 1100°C for 20 hr in air. The deformation rate was $2 \cdot 10^{-5}$ m · min^{-1}.